REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	29 Oct 01	Final Report 07 Jul 00 - 06 Jul 01

4. TITLE AND SUBTITLE
Stress Effects in Bulk Metallic Glasses

5. FUNDING NUMBERS
DAAD19 00 1 0379

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
California Institute of Technology

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
US Army Research Office

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
40063.7- MS

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
This project initiated a systematic study of the internal stresses in bulk metallic glasses. It involved internal stresses due to interactions between reinforcements and matrix in bulk metallic glass composites as well as residual stresses due to the thermal tempering of bulk metallic glasses.

20030605 190

14. SUBJECT TERMS

15. NUMBER OF PAGES
5

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

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Sincerely,

Ersan Ustundag

Enclosure 3

FINAL PROGRESS REPORT

Statement of the Problem Studied

This project initiated a systematic study of the internal stresses in bulk metallic glasses (BMGs). It involved internal stresses due to interactions between reinforcements and matrix in BMG composites as well as residual stresses due to the thermal tempering of BMGs.

Summary of the Most Important Results

(a) Internal Stresses due to Thermal Tempering of Bulk Metallic Glasses

The viscoelastic nature of BMGs, their low thermal conductivity and the relatively fast cooling employed in their processing lead to thermal tempering. In this process, compressive stresses develop on the surface balanced by tension in the interior. We have adapted an "instant freezing model" originally developed for silicate-based glasses to calculate these stresses as a function of processing conditions and specimen dimensions (see Fig. 1) [4][†]. (Here, the Biot number is given by $Bi = hl/k$, where h is the heat transfer coefficient, l is the half thickness of an infinite plate and k is thermal conductivity.) As cooling rate (and hence h) and/or specimen thickness increase progressively larger compressive stresses are predicted on the specimen surface (Fig. 1). In the meantime, the mid-plane tension remains relatively constant over roughly the same part of the plate. This means larger stress gradients are generated near the plate surfaces as the value of surface compression increases.

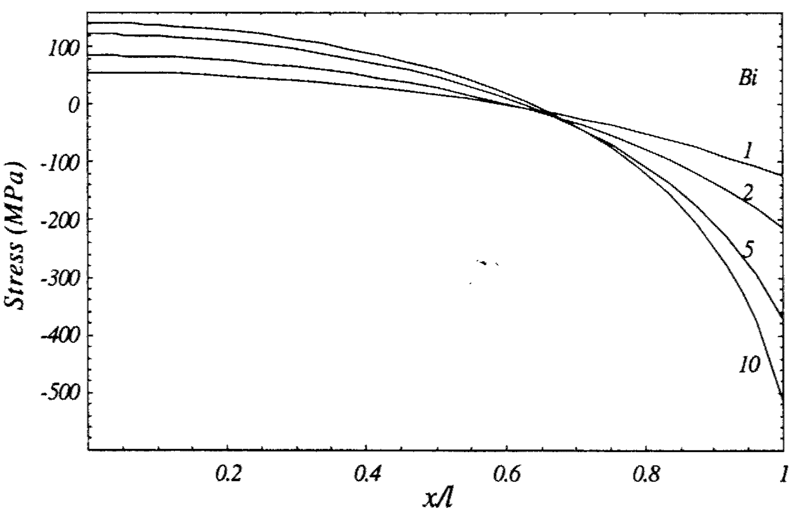


Figure 1. The residual stress profiles across the *half* thickness of a BMG plate as a function of Biot number (from ref. [1]).

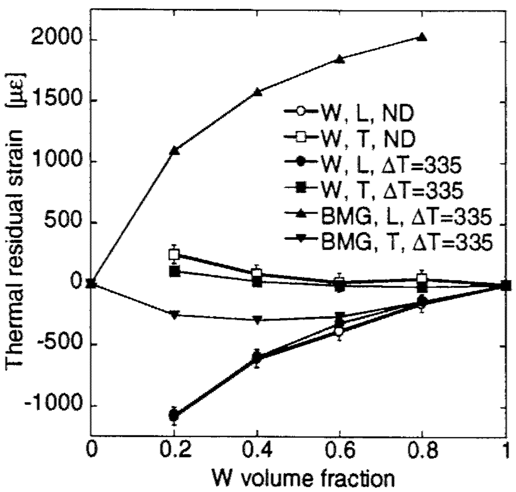
Although it cannot estimate the transient stresses during processing, this model is known to be reasonably accurate in predicting the final values of tempering-induced residual stresses. To check its accuracy, we have initiated a systematic experimental study to measure these stresses using mechanical relaxation methods such as layer removal, crack compliance and hole drilling [4,2]. Preliminary results obtained from the layer removal method suggest that the model predictions are reasonably close to experimental values of the residual stresses due to thermal tempering [1]. On the other hand, residual stresses obtained by the crack compliance method suggest higher variability in thermal tempering as a function of processing conditions [2]. The crack compliance studies involving different BMG plates are currently underway.

In our other current work, we have started looking into the viscoelastic properties of BMGs so that more advanced models of tempering can be employed in stress calculations. These models are not only more accurate in predicting the final stress values, but they can also estimate transient stresses that occur during processing.

(b) Internal Stresses in Bulk Metallic Glass Matrix Composites

These stresses originate from the interactions between the BMG matrix and reinforcements. The first source is the coefficient of thermal expansion (CTE) mismatch between the two constituents. As the BMG composite is cooled after casting, significant residual stresses can develop due to this mismatch. We have investigated this phenomenon in W-fiber/BMG-matrix composites (Section i). The second source of internal

[†] Reference numbers refer to the publication list in the Bibliography section.



gure 2. Comparison of FE calculations ıdicated by ΔT=335) with neutron diffraction D) data from W fibers. The strains in the BMG ıtrix are FE predictions. (L: longitudinal, T: nsverse). From ref. [3].

stress is the elastic and plastic incompatibility between the matrix and reinforcements. When a composite is subjected to an applied stress, this incompatibility leads to internal stress development from which one can deduce the *in-situ* mechanical behavior of the reinforcements. The last two sections describe the results of our work on W/BMG and Ta/BMG particulate-reinforced composites as well as preliminary data from the new "β phase"/BMG composites.

i. Residual Stresses in W/BMG Composites

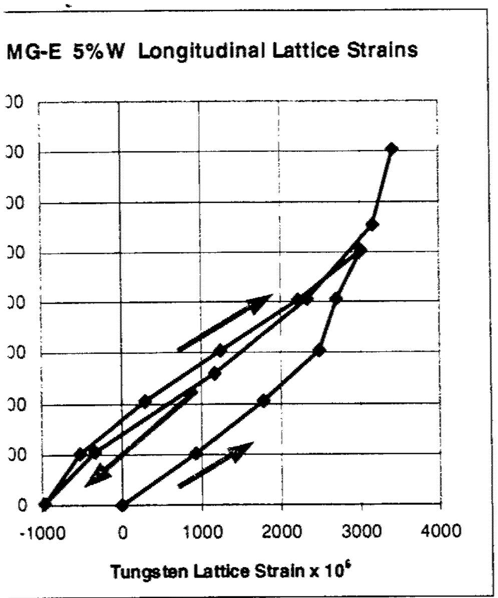
W-fiber/BMG-matrix composites have been developed at Caltech (by W.L. Johnson and co-workers) as suitable materials for kinetic penetrators. We studied the thermal residual stresses in these composites using neutron diffraction (ND) and finite element modeling (FEM) [3]. The CTE of BMG is larger than that of W; therefore, upon cooling, the W is expected to be in longitudinal compression while the BMG matrix will be put in tension along the same direction. Our ND measurements of strains in W fibers in four W/BMG composites with fiber volume fractions of 20, . 60 and 80% confirmed this prediction (see Fig. 2). We then used the ND data to develop a FE model that ll estimate the stresses and strains in the BMG matrix. It turned out that a simple elastic model is accurate ɔugh to estimate the thermal residual stresses/strains in these composites. The "freezing temperature" below ıich stress generation starts during cooling was found to be just below the glass transition temperature of this ⁄IG alloy (Vitreloy 1), about 355°C [3]. The overall result of this study is that both constituents of these W-er/BMG composites practically behave as elastic materials during cooling after casting.

Our current study on these materials involves *in-situ* compression tests using the new neutron ɛctrometer (SMARTS) at Los Alamos Neutron Science Center. This instrument has enough loading capacity reach the yield point of these composites (around 2 GPa). This way we expect to learn more about the *in-situ* ·chanical behavior of the reinforcements, especially their yield strength. We will also study other fiber-nforced composites with Ta, steel and Mo fibers.

ii. *In-Situ* Deformation of Reinforcements in W/BMG and Ta/BMG Composites

We performed X-ray diffraction (XRD) experiments with these particulate-reinforced composites to lerstand the deformation behavior of the reinforcements. We employed high-energy (~ 65 keV) X-rays to .ure complete penetration through specimens while applying tension; therefore, the strain data obtained was a lk average within the sampling volume. The experiments were performed at the Advanced Photon Source in laboration with D.C. Dunand from Northwestern University. Additional details can be found in refs. [4,5].

Fig. 3 shows a typical stress-strain plot from a 5% W/BMG composite. Qualitatively similar results re also obtained from 10% W/BMG and 5% Ta/BMG composites [4,5]. In Fig 3, the W particles are first ːn to deform elastically up to about 600 MPa applied composite stress. (Note that the thermal residual ɛsses/strains are not included in this figure.) At about 1000 MPa, the specimen was unloaded while ·asuring the lattice strains in W. After complete unloading, a compressive residual strain (about −1000 με) .s observed in W. This is likely due to the plastic mismatch between the particles and the matrix. In other ırds, the yielding of W probably led to a change in its shape, which upon unloading of the elastic BMG matrix ulted in a compressive residual strain in W. When the specimen was pulled again, the W particles were seen experience strain hardening since they did not yield until about 1000 MPa (Fig. 3). We note that the slopes loading/unloading plots are roughly the same suggesting that the W/BMG interfaces were intact on average 1 no significant debonding occurred after the yielding of the W particles. This observation confirmed the ;h strength of the W/BMG interface.



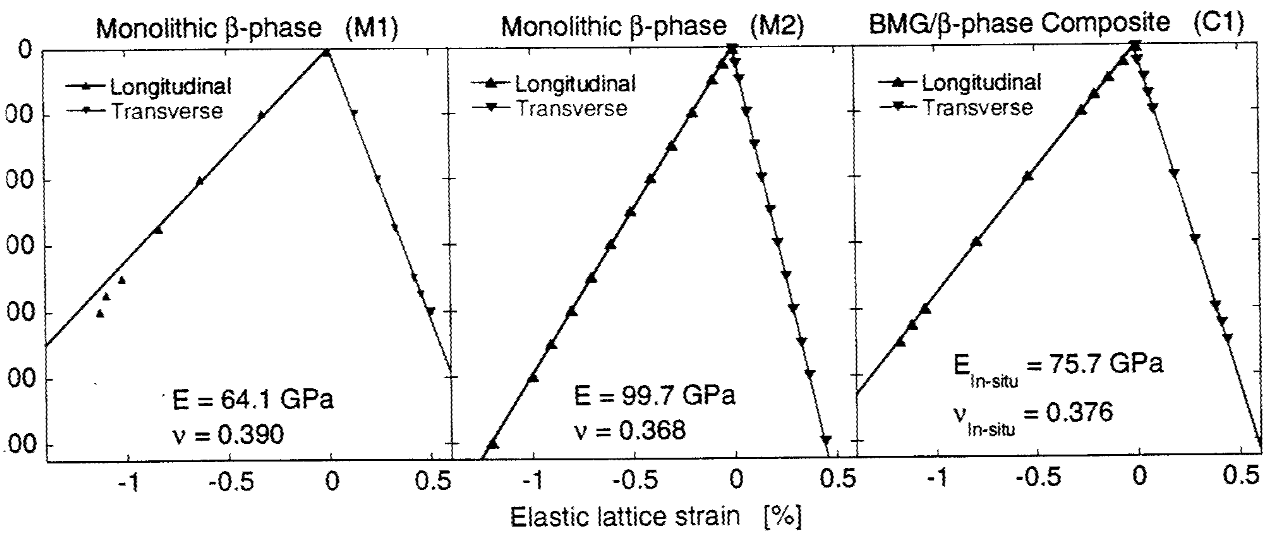
e **3.** Lattice strain development in W les during a tensile loading/unloading of a 5% W/BMG composite. Adapted ef. [4].

Using these XRD data we calculated the *in-situ* yield strengths of all reinforcements and found that they were approximately the same as the literature values [4,5]. This result suggested that the inclusion of ductile particles in a hard, elastic BMG matrix did not lead to any significant hardening of the particles. The overall conclusion of this study was that the ductile reinforcements were usually the first phase to yield in a BMG composite. This yielding would somehow initiate "plastic" deformation in the BMG matrix via shear band formation. The details of the micromechanics of shear band/reinforcement interaction are still not known. This is the subject of our current investigations.

iii. Investigation of "β Phase"/BMG Composites

These composites form when dendrides of a mostly Zr and Ti alloy with BCC structure precipitate during the casting of special BMG alloys. Since they form *in situ*, the size and spacing of these "β phase" precipitates can be manipulated allowing microstructure, and therefore, mechanical property control. Indeed, recent work by W.L. Johnson and co-workers have shown that the "β phase"/BMG composites are significantly more ductile compared to monolithic BMG

We have recently initiated a systematic study on these composites to understand how the "β phase" nprove the mechanical properties of BMGs. First experiments involved *in-situ* compression tests using diffraction [6]. Two "β phase" monoliths and a composite were studied (see Fig. 4). It was seen that e ductility and modulus of the "β phase" was highly sensitive to its heat treatment. While an as-cast en (M1 in Fig. 4) yielded around 600 MPa, its slightly heat-treated counterpart (M2) was elastic until it



re **4.** Comparison of the compressive stress-strain behavior of two "β phase" monoliths and a "β phase"/BMG osite. The strains were measured using neutron diffraction. The monoliths had the same chemical osition as that found in the "β phase" inside the composite. They were nominally identical except that M2 heat treated at 350°C for 15 min. The elastic constant data shown in the figure were calculated by fitting ht lines to the elastic portion of the stress-strain plots. Adapted from ref. [6].

failed in a brittle manner around 1425 MPa. The Young's modulus of the "β phase" increased from 64 GPa (M1) to about 100 GPa (M2). The ND results also showed that while M2 was nearly isotropic in its elastic constants (anisotropy ratio, AI, was calculated to be around 1.6; 1.0 would be perfectly isotropic), M1 was very anisotropic with an AI value of 5.5. M1 was also seen to be rather soft against shear [6].

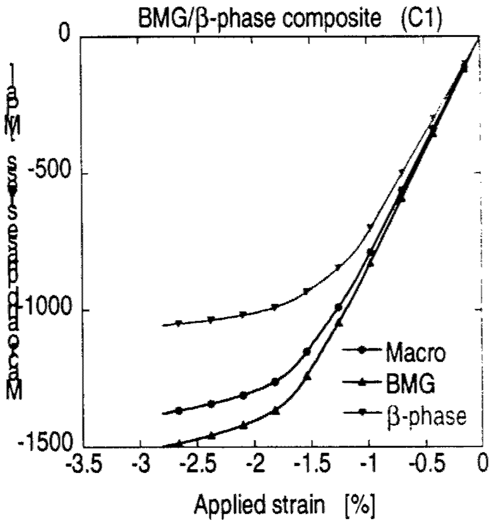


Figure 5. Self-consistent model calculation of load sharing in "β phase"/BMG composite [6]. The "β phase" is seen to yield around 700 MPa while the BMG matrix yields above 1200 MPa.

The "β phase" in the composite was observed to be elastic up to about 700 MPa applied stress (see Fig. 5). This again suggests that it is the reinforcement that yields first inducing plasticity in the matrix later. These results also suggest that the "β phase" properties can be modified dramatically by heat treatment and that one has to be careful in assuring that the ductile version is obtained in the composite to assure high overall toughness. The reason for the changes in "β phase" properties is not known at present time. However, ordering in its crystal structure is a good possibility and our current work involves extensive TEM and ND studies to confirm this.

List of Papers Submitted or Published

(a) Papers Published in Peer-Reviewed Journals

1. D. Dragoi, E. Üstündag, B. Clausen and M. A. M. Bourke, "Investigation of Thermal Residual Stresses in Tungsten-Fiber/Bulk Metallic Glass Composites," *Scripta Mater.*, **45** (2), 245-252 (2001).
2. C. C. Aydiner, E. Üstündag and J. C. Hanan, "Thermal Tempering Analysis of Bulk Metallic Glass Plates Using an Instant Freezing Model," in print: *Metall. Mater. Trans.*, **32A**, (2001).

(b) Papers Published in Non-Peer-Reviewed Journals or in Conference Proceedings (peer reviewed)

1. E. Üstündag, C. C. Aydiner, D. Dragoi, B. Clausen, M. A. M. Bourke and R. A. Winholtz, "Residual Stresses in Bulk Metallic Glasses and Composites," in: Proceedings of the Sixth International Conference on Residual Stresses (ICRS-6), v. **1**, IOM Communications, London, UK (2000), pp. 155-162.
2. D. Dragoi, E. Üstündag, B. Clausen and M. A. M. Bourke, "Residual Stresses in Tungsten / Bulk Metallic Glass Composites," in print: *Adv. X-Ray Anal.*, **44** (2000).
3. D. K. Balch, E. Üstündag and D. C. Dunand, "Synchrotron X-ray Diffraction Measurement of Reinforcement Strains in Uniaxially Stressed Bulk Metallic Glass Composites," in print: MRS Symp. Proc., vol. **678** (2001).

(c) Papers Presented at Meetings, but not Published in Conference Proceedings

1. E. Üstündag, "Internal Stresses in Composites (*Invited*)," High-Energy X-ray Diffraction Workshop, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, March 2001.
2. E. Üstündag, D. K. Balch and D. C. Dunand, "Investigation of Load-Transfer in Ta-Reinforced Bulk Metallic Glasses Using High-Energy X-Ray Diffraction," 50th Annual Denver X-Ray Conference, Steamboat Springs, CO, July 2001.
3. S. Y. Lee, B. Clausen, E. Üstündag, D. W. Brown and M.A.M. Bourke, "Mechanical Behavior of *In-Situ* Formed Bulk Metallic Glass Matrix Composites," (poster), Los Alamos Neutron Science Center User Group Meeting, Los Alamos, NM, August 2001.
4. B. Clausen, S. Y. Lee, E. Üstündag, D. W. Brown and M.A.M. Bourke, "Thermal Residual Stresses in Tungsten-Fiber/Bulk Metallic Glass Matrix Composites," (poster), Los Alamos Neutron Science Center User Group Meeting, Los Alamos, NM, August 2001.

(d) Manuscripts Submitted, but Not Published:

1. E. Üstündag, D. Dragoi, B. Clausen, D. W. Brown, M.A.M. Bourke, D.K. Balch and D.C. Dunand, "Internal Stresses in Bulk Metallic Glass Matrix Composites," submitted to MRS Symp. Proc., (2000).

(e) Manuscripts in Preparation

1. D. Balch, E. Üstündag and D. C. Dunand, "Load Transfer during Tensile Loading of Bulk Metallic Glass Composites," to be submitted to *Acta Mater.*, (2001).
2. B. Clausen, S. Y. Lee, E. Üstündag, C. P. Kim, J. C. Hanan, D. W. Brown and M.A.M. Bourke, "Compressive Loading of *In-Situ*-Formed Bulk Metallic Glass Composites," to be submitted to *Acta Mater.*, (2001).
3. C. C. Aydiner, E. Üstündag and M. B. Prime, "Measurement of Residual Stresses in Bulk Metallic Glasses using the Crack Compliance Method," to be submitted to *J. Non-Cryst. Solids*, (2001).

(f) Technical Reports Submitted to ARO: N/A

Scientific Personnel

- Prof. Ersan Üstündag, principal investigator.
- Dr. Bjørn Clausen, senior postdoctoral scholar.
- Dr. Danut Dragoi, postdoctoral scholar.
- C. Can Aydiner, graduate student.
- Seung-Yub Lee, graduate student.
- Jay C. Hanan, graduate student.

Report of Inventions: N/A

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1. C. C. Aydiner, E. Üstündag and J. C. Hanan, "Thermal Tempering Analysis of Bulk Metallic Glass Plates Using an Instant Freezing Model," in print: *Metall. Mater. Trans.*, **32A**, (2001).
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3. D. Dragoi, E. Üstündag, B. Clausen and M. A. M. Bourke, "Investigation of Thermal Residual Stresses in Tungsten-Fiber/Bulk Metallic Glass Composites," *Scripta Mater.*, **45** (2), 245-252 (2001).
4. D. K. Balch, E. Üstündag and D. C. Dunand, "Synchrotron X-ray Diffraction Measurement of Reinforcement Strains in Uniaxially Stressed Bulk Metallic Glass Composites," in print: MRS Symp. Proc., vol. **678** (2001).
5. D. Balch, E. Üstündag and D. C. Dunand, "Load Transfer during Tensile Loading of Bulk Metallic Glass Composites," to be submitted to *Acta Mater.*, (2001).
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